

- (21) Application No. 47202/74 (22) Filed 31 Oct. 1974  
(31) Convention Application No. 412 534  
(32) Filed 5 Nov. 1973 in  
(33) United States of America (US)  
(44) Complete Specification published 12 May 1976  
(51) INT CL<sup>2</sup> C25D 3/56  
(52) Index at acceptance C7B 1B 1E 1G 1Q 1R 1T 1V  
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(54) IMPROVEMENTS IN OR RELATING TO THE  
ELECTRODEPOSITION OF NICKEL/IRON OR  
NICKEL/IRON ALLOYS

(71) We, M. & T. CHEMICALS INC., a corporation organized and existing under the laws of the State of Delaware, United States of America, with executive offices at American Lane, Greenwich, Connecticut, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the use of a new electroplating additive to improve the plating of iron-containing alloys of nickel, and nickel-cobalt.

Because of the much lower cost of iron and its salts as contrasted to that of nickel and cobalt and their salts it would be highly desirable to electrodeposit alloys of nickel or nickel and cobalt with iron containing an appreciable iron content thereby reducing metal and salt costs. It has been found that of the two common valence forms of iron,  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$ , the ferrous of  $\text{Fe}^{+2}$  form is the optimum one for permitting plating of these alloys although the baths generally can tolerate low concentrations of  $\text{Fe}^{+3}$  iron. The problem with plating of these iron alloys, however, has been that, due to the presence of excessive concentrations of  $\text{Fe}^{+3}$ , which may form by air oxidation or anodic oxidation of  $\text{Fe}^{+2}$ , the  $\text{Fe}^{+3}$  tends to precipitate out as basic salts which not only objectionably tend to clog anode bags and filters but also codeposit to give unsatisfactory deposits. The latter may show haziness or localized dullness, especially on "shelf" areas, or, if the suspended ferric basic salt concentration is excessively high, an overall micro-mound formation often referred to as "orange-peel". This problem of precipitation of basic ferric salts has therefore to date made the commercial electrodeposition of alloys of iron with nickel or nickel and cobalt impractical.

Also in the art of nickel or nickel and cobalt or cobalt plating, either for functional or decorative and corrosion-resistance applications, ferric or  $\text{Fe}^{+3}$  iron presents the same problems. The iron in such baths may not be intentionally added, since the purpose is not to plate a nickel-iron or nickel-cobalt-iron or cobalt-iron alloy, but may be introduced from water used for bath make-up and replenishment, from iron impurity in nickel cobalt or nickel-cobalt anodes, used, from salts used for bath make-up and replenishment, and from attack of the electrolyte on ferrous basis metals being plated, especially in very low cathode current density areas, or which may drop into the tank from racks or fixtures holding the parts. If the iron, which initially may enter the bath as ferrous,  $\text{Fe}^{+2}$ , iron is partially or completely oxidized to ferric,  $\text{Fe}^{+3}$ , state, even in concentrations of, say 25 to several hundred milligrams per litre, it will form a basic ferric salt precipitate which will cause the problems previously enumerated.

To overcome or mitigate the problems associated with formation of basic ferric salt precipitates there are two possible approaches. One would be to use a reducing agent which would tend to substantially keep all of the iron in the  $\text{Fe}^{+2}$  state. Although there are available such reducing agents, most tend to be unstable, form harmful reduction products or adversely affect deposit characteristics or general bath control and performance.

The better approach would be to incorporate in the plating bath an additive which will solubilize  $\text{Fe}^{+3}$  by a complexing or chelating action. To be practical such an additive must have the following characteristics:

1. It must be relatively stable to electrolysis i.e. reducing (cathode) and oxidation (anode) conditions.
2. It must be compatible with other additives which are used singly or in combination as grain-refining or brightening agents i.e. it must not adversely affect the performance of these other additives.
3. It must be relatively inexpensive and not be critical in its permissible concentration limits.
4. It must tolerate fairly wide fluctuations in bath  $\text{Fe}^{+2}$  concentration.

There are some complexing compounds which may have some of the above characteristics but generally they are found deficient in others. For example the citrate, tartrate and gluconate anions tend to keep  $\text{Fe}^{+3}$  complexed and solubilized but they are limited in the extremely important characteristic of the  $\text{Fe}^{+2}$  concentrations which they may tolerate when the prime purpose is to plate alloys which have an iron content substantially higher than would be introduced from normally encountered impurity concentration levels.

If certain  $\text{Fe}^{+2}$  concentration limits, comprising some which one would normally expect to encounter, are exceeded the deposits may exhibit such undesirable characteristics as blotchiness, poor adhesion, spontaneous cracking, and non-uniformity in lustre and general appearance.

It has been discovered that the glucoheptonate anion has all of the above desirable characteristics.

It is an object of this invention to improve the electrodeposition of alloys of nickel and iron and alloys of nickel-cobalt-iron.

According to the invention we provide a process for electrodepositing on a substrate an alloy of iron and nickel or an alloy of iron, cobalt and nickel comprising passing an electric current from an anode to a cathode through an aqueous acidic plating solution containing at least one ferrous compound and at least one nickel compound with or without at least one cobalt compound, the plating solution also containing at least one compound providing glucoheptonate anion in a concentration of 2 grams per litre to 50 grams per litre. The plating solution may contain one or more of the following: nickel chloride, nickel sulphate, nickel sulphamate, cobalt chloride, cobalt sulphamate, cobalt sulphate, ferrous sulphate, ferrous chloride and ferrous sulphamate. Preferably the plating solution contains at least one compound, preferably a salt, providing glucoheptonate anion in a concentration of 10 grams per litre to 50 grams per litre.

According to another aspect of the invention we provide an aqueous acidic plating solution as defined in the preceding paragraph.

The plating solution may contain one or more additives chosen from:

- (a) primary brighteners;
- (b) secondary brighteners;
- (c) secondary auxiliary brighteners;
- (d) anti-pitting agents.

In the bath of this invention cobalt in the form of cobalt sulphate or cobalt chloride may be substituted for a portion of the nickel to obtain a ternary Ni-Co-Fe alloy. However, because of the relatively high cost of cobalt, it is preferred to plate only an alloy of Ni and Fe for maximum economy of operation.

Although functional or decorative and corrosion-resistant deposits of cobalt may be plated, such as by the process disclosed in our U.K. Specification 1,337,381, application Serial No. 884,050, which may contain relatively low iron contents, say less than 2% by weight, attempts to plate cobalt-iron alloys where the iron is substantially higher, have not been successful to date, particularly where dull matte, semi-bright or bright deposits have been desired having thicknesses of the order of magnitude generally used for decorative and corrosion-resistant applications. For certain functional applications, such as for magnetic and electronic purposes, where only deposit physical properties are of importance and good appearance may not be of primary concern and, also, where very low deposit thicknesses are used, such higher iron content cobalt-iron alloys may be usefully plated.

The glucoheptonate anion is preferably added as the readily commercially available and relatively inexpensive sodium glucoheptonate. This material is relatively pure as obtainable commercially and should be slightly off-white or light cream coloured fine crystals. It may also be obtained in the form of a dark-coloured solution of sodium salts of glucoheptonate and other by-products of manufacture; this form is not preferred since it may introduce into the bath objectionable organic impurities which may adversely affect deposit physical

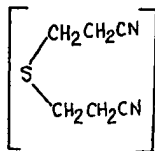
properties and overall bath performance. The glucoheptonate anion may also be introduced as an alkali metal salt, preferably sodium, of boroglucoheptonate which is also commercially available in the form of its crystalline, relatively pure sodium salt and which on addition to the bath supplies the glucoheptonate and borate anions, the latter of which is generally present in relatively high concentration and added as boric acid for buffering and other purposes. The glucoheptonate may also be added as the salt of the other bath-compatible cations besides sodium (such as potassium, nickel, magnesium, lithium, etc.) but such salts are not usually commercially available and would be more expensive if they had to be synthesized.

If an alloy of nickel and iron is desired which need not be brilliant or well levelled but still very sound and ductile for other than decorative purposes the use of a primary and a secondary auxiliary brightener may be eliminated and only an anti-pitting agent and sulpho-oxygen compound, preferably saccharin, may be used. For bright, well-levelled alloy plating, primary brighteners such as diethoxylated 2 butyne-1,4-diol or dipropoxylated 2 butyne-1,4-diol may be used in cooperation with a sulpho-oxygen secondary brightener, preferably saccharin, a secondary auxiliary brightener and an anti-pitting agent. If full brightness and levelling are not desired a fairly lustrous deposit with fair levelling may be obtained using as a primary brightener a nitrogen heterocyclic compound such as N-allyl quinolinium bromide at a concentration of about 5 to 20 mg/l in cooperation with a sulpho-oxygen secondary brightener, a secondary auxiliary brightener and an anti-pitting agent.

The substrates on which the nickel-iron containing or nickel-cobalt-iron containing electrodeposits of this invention are applied may be metal or metal alloys such as are commonly electrodeposited on and used in the art of electroplating, examples of substrates being nickel, cobalt, nickel-cobalt, copper, tin and brass. Other typical substrate basis metals from which articles to be plated are manufactured may include ferrous metals such as steel; copper; tin and alloys thereof such as with lead; alloys of copper such as brass, bronze, etc.; zinc, particularly in the form of zinc-base die castings, all of which may bear plates of other metals, such as copper, etc. Basis metal substrates may have a variety of surface finishes depending on the final appearance desired, which in turn depends on such factors as lustre, brilliance, levelling, thickness, etc. of the nickel-iron or nickel-cobalt-iron containing electroplate applied on such substrates.

The term "primary brightener" as used herein is meant to include plating additive compounds such as reaction products of epoxides with *alpha*-hydroxy acetylenic alcohols such as diethoxylated 2 butyne-1,4-diol or dipropoxylated 2 butyne-1,4-diol, other acetylenics, N-heterocyclics, active sulphur compounds and dye-stuffs. Specific examples of such plating additives are:

- 1,4-di-( $\beta$ -hydroxyethoxy)-2-butyne
- 1,4-di-( $\beta$ -hydroxy-*p*-chloropropoxy)-2-butyne
- 1,4-di-( $\beta$ -*p*-epoxypropoxy)-2-butyne
- 1,4-di-( $\beta$ -hydroxy-*p*-butenoxy)-2-butyne
- 1,4-di-(2'-hydroxy-4'-oxa-6'-heptenoxy)-2-butyne
- N-1,2-dichloropropenyl pyridinium chloride
- 2,4,6-trimethyl N-propargyl pyridinium bromide
- N-allyl quinaldinium bromide
- N-allyl quinolinium bromide
- 2-butyne-1,4-diol
- propargyl alcohol
- 2-methyl-3-butyne-2-ol
- thiodipropionitrile



thiourea  
phenosafranin  
fuchsin

When used alone or in combination, a primary brightener may produce no visual effect on the electrodeposit, or may produce semi-lustrous, fine-grained deposits. However, best results are obtained when primary brighteners are used with either a secondary brightener, a secondary auxiliary brightener, or both in order to provide optimum deposit lustre, rate of brightening, levelling, bright plate current density range, low current density coverage, etc.

The term "secondary brightener" as used herein is meant to include aromatic sulphonates, sulphonamides, sulphonimides and sulphinates. Specific examples of such plating additives are:

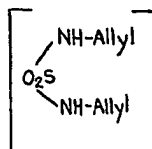
1. saccharin
2. trisodium 1,3,6-naphthalene trisulphonate
3. sodium benzene monosulphonate
4. dibenzene sulphonimide
5. sodium benzene monosulphinate.

Such plating additive compounds, which may be used singly or in suitable combinations, have one or more of the following functions:

1. To obtain semi-lustrous deposits or to produce substantial grain-refinement over the usual dull, matte, grainy, non-reflective deposits from additive free baths.
2. To act as ductilizing agents when used in combination with other additives such as primary brighteners.
3. To control internal stress of deposits, generally by making the stress desirably compressive.
4. To introduce controlled sulphur contents into the electrodeposits to desirably affect chemical reactivity, potential differences in composite coating systems, etc. thereby decreasing corrosion, better protecting the basis metal from corrosion, etc.

The term "secondary auxiliary brightener" as used herein is meant to include aliphatic or aromatic-aliphatic olefinically or acetylenically unsaturated sulphonates, sulphonamides or sulphonimides. Specific examples of such plating additives are:

1. sodium allyl sulphonate
2. sodium-3-chloro-2-butene-1-sulphonate
3. sodium  $\beta$ -styrene sulphonate
4. sodium propargyl sulphonate
5. monoallyl sulphamide ( $\text{H}_2\text{N}-\text{SO}_2-\text{NH}-\text{CH}_2-\text{CH}=\text{CH}_2$ )
6. diallyl sulphamide



7. allyl sulphonamide.

Such compounds, which may be used singly (usual) or in combination have all of the functions given for the secondary brighteners and in addition may have one or more of the following functions:

1. They may act to prevent or minimize pitting (probably acting as hydrogen acceptors).
2. They may cooperate with one or more secondary brighteners and one or more primary brighteners to give much better rates of brightening and levelling than would be possible to attain with any one or any two compounds selected from all three of the classes:
  - (1) primary brightener;
  - (2) secondary brightener; and
  - (3) secondary auxiliary brightener used either alone or in combination.
3. They may condition the cathode surface by catalytic poisoning, etc. so that the rates of consumption of cooperating additives (usually of the primary brightener type) may be substantially reduced, making for better economy of operation and control.

Among the secondary auxiliary brighteners one may also include ions or compounds of certain metals and metalloids such as zinc, cadmium or selenium which, although they are not generally used at present, have been used to augment

deposit lustre, etc. Other cooperating additives of organic nature which may be useful are the compounds of U.S. Patent Specification No. 3,697,391 i.e. typically, sodium formaldehyde bisulphite, the function of which is to make baths more tolerant to primary brightener concentrations, to increase tolerance toward metallic impurities such as zinc, etc.

The term "anti-pitting agent" as used herein is meant to include a material (different from and in addition to the secondary auxiliary brightener) which functions to prevent or minimize gas pitting. An anti-pitting agent may also function to make the baths more compatible with contaminants such as oil, grease, etc. by their emulsifying, dispersing, solubilizing, etc. action on such contaminants and thereby promote attaining of sounder deposits. Anti-pitting agents are optional additives which may or may not be used in combination with one or more members selected from the group consisting of a primary brightener, a secondary brightener, and a secondary auxiliary brightener. Preferred anti-pitting agents include sodium lauryl sulphate, sodium lauryl ether sulphate and sodium di-alkyl-sulphosuccinates.

Typical nickel-iron-containing and nickel-cobalt-iron-containing bath compositions which may be used in combination with effective amounts of about 0.005—0.2 gram per litre of primary brightener, with about 1.0—30 grams per litre of secondary brightener, with about 0.5—10 grams per litre of secondary auxiliary brightener, and with about 0.05—1 gram per litre of anti-pitting agent, described herein, are summarized below. Combinations of primary brighteners and of secondary brighteners may also be used with the total concentration of members of each class coming within the typical concentration limits stated.

Typical aqueous nickel-containing electroplating baths (which may be used in combination with effective amounts of cooperating additives) include the following wherein all concentrations are in grams per litre (g/l) unless otherwise indicated.

Salts to make up the bath are of the types generally used for nickel and cobalt plating i.e. the sulphates and chlorides, usually combinations thereof. Ferrous iron may be added as ferrous sulphate or ferrous chloride, or ferrous sulphamate, preferably the sulphate which is easily available at low cost and good degree of purity (as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ).

TABLE I.  
AQUEOUS NICKEL-CONTAINING ELECTROPLATING BATHS.

Component	Minimum	Maximum	Preferred
nickel sulphate	200	500	300
nickel chloride	30	80	45
ferrous sulphate	5	80	40
boric acid	35	55	45
pH (electrometric)	3	5	4

A typical sulphamate-type nickel plating bath which may be used in the practice of this invention may include the following components:

TABLE II.

Component	Minimum	Maximum	Preferred
nickel sulphamate	330	400	375
nickel chloride	15	60	45
ferrous sulphamate	5	80	40
boric acid	35	55	45
pH (electrometric)	3	5	4

A typical chloride-free sulphate-type nickel plating bath which may be used in the practice of this invention may include the following components:

TABLE III.

Component	Minimum	Maximum	Preferred
nickel sulphate	300	500	400
ferrous sulphate	5	80	40
boric acid	35	55	45
pH (electrometric)	2.5	4	3—3.5

A typical chloride-free sulphamate-type nickel plating bath which may be used in the practice of this invention may include the following components:

TABLE IV.

Component	Minimum	Maximum	Preferred
nickel sulphamate	300	400	350
ferrous sulphamate	5	80	40
boric acid	35	55	45
pH (electrometric)	2.5	4	3—3.5

It will be apparent that the above baths may contain compounds in amounts falling outside the preferred minimum and maximum set forth, but most satisfactory and economical operation may normally be effected when the compounds are present in the baths in the amounts indicated. A particular advantage of the chloride-free baths of Tables III and IV, *supra*, is that the deposits obtained may be substantially free of tensile stress and may permit high speed plating involving the use of high speed anodes.

The following is an aqueous cobalt-nickel-iron-containing electroplating bath in which the combination of effective amounts of one or more cooperating additives according to a preferred mode of this invention will result in beneficial effects.

TABLE V.  
AQUEOUS COBALT-NICKEL-IRON-CONTAINING ELECTROPLATING BATH.

(All concentrations in g/l unless otherwise noted).

Cobalt-Nickel Alloy Bath	Maximum	Minimum	Preferred
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	400	200	300
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	225	15	80
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	75	15	60
$\text{H}_3\text{BO}_3$	50	37	45

Ferrous Sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) is included in the foregoing bath in a concentration of about 5 g/l to 80 g/l.

The pH of all of the foregoing illustrative aqueous iron-nickel-containing and nickel-cobalt-iron-containing compositions may be maintained during plating at pH values of 2.0 to 4.0, and preferably from 3.0 to 3.5. During bath operation, the pH may normally tend to rise and may be adjusted with acids such as hydrochloric acid or sulphuric acid.

Operating temperature ranges for the above baths may be about 30 to 70°C. with temperatures within the range of 45 to 65°C. preferred.

Agitation of the above baths during plating may consist of solution pumping, moving cathode rod, air agitation or combinations thereof.

- 5 Anodes used in the above baths may consist of the particular single metals being plated at the cathode such as iron and nickel, for plating nickel-iron or nickel, cobalt, and iron for plating nickel-cobalt-iron. The anodes may consist of the separate metals involved suitably suspended in the bath as bars, strips or as small chunks in titanium baskets. In such cases the ratio of the separate metal anode areas is adjusted to correspond to the particular cathode alloy composition desired. For plating binary or ternary alloys one may also use as anodes alloys of the metals involved in such a per cent weight ratio of the separate metals as to correspond to the per cent weight ratio of the same metals in the cathode alloy deposits desired. These two types of anode systems will generally result in a fairly constant bath metal ion concentration for the respective metals. If with fixed metal ratio alloy anodes there does occur some bath metal ion imbalance, occasional adjustments may be made by adding the appropriate corrective concentration of the individual metal salts. All anodes or anode baskets are usually suitably covered with cloth or plastic bags of desired porosity to minimize introduction into the bath of metal particles, anode slime, etc. which may migrate to the cathode either mechanically or electrophoretically to give roughness in cathode deposits.
- 10
- 15
- 20 The following examples are submitted for the purpose of comparison and illustration.

#### EXAMPLE 1 (Comparative).

- 25 A nickel-iron electroplating bath composition was prepared by combining in water the following ingredients to provide the indicated concentrations.
- |    |  |         |    |
|----|--|---------|----|
|    | nickel sulphate  | 300 g/l |    |
|    | nickel chloride  | 60 g/l  |    |
|    | boric acid   | 45 g/l  |    |
| 30 | ferrous sulphate   | 60 g/l  | 30 |
|    | sodium saccharinate (0.6H <sub>2</sub> O)  | 4.0 g/l |    |
|    | sodium allyl sulphonate  | 2.3 g/l |    |
|    | diethoxylated 2 butyne-1,4-diol  | 50 mg/l |    |
| 35 | sodium di-n-hexyl-sulphosuccinate/0.25 g/l   |         |    |
|    | rochelle salt (KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·4H <sub>2</sub> O) | 60 g/l  | 35 |
|    | pH   | 3.8     |    |

- 40 A polished brass panel was scribed with a horizontal single pass of 2/0 grit emery to give a band width of about 1 cm. at a distance of about 2.5 cm. from the bottom of the panel. After cleaning the panel, including the use of a thin cyanide copper strike to assure excellent physical and chemical cleanliness, it was plated in a 267 ml. Hull Cell, at a 2 ampere cell current for 10 minutes, at a temperature of 50°C. and using magnetic stirring. The Hull Cell deposit was brilliant and fairly well levelled with fair low current density coverage; on bending the high current density edge deposit peeling occurred.
- 45 On adding 20 g/l more of ferrous sulphate a bright deposit was obtained but with two large, blotchy, hazy, very thin deposit scattered areas.

#### EXAMPLE 2 (Comparative).

- 50 Example 1 was repeated using 60 g/l potassium citrate monohydrate in place of the rochelle salt. The deposit was generally bright but with two large, scattered, striated and hazy, thin deposit areas.
- 50 On adding 20 g/l more of ferrous sulphate a poor blotchy, striated, hazy and dull deposit was obtained.

#### EXAMPLE 3 (Comparative).

- 55 Example 1 was repeated using 60 g/l sodium gluconate in place of the rochelle salt. A non-uniformly hazy deposit was obtained with poor levelling.
- 55 On adding 20 g/l more of ferrous sulphate a non-uniformly hazy and blotchy deposit with spontaneous cracking in the high current density end of the range was obtained.

#### EXAMPLE 4 (Invention).

- 60 Example 1 was repeated using 10 g/l sodium glucoheptonate in place of the rochelle salt. A bright, quite well-levelled, ductile deposit with good low current
- 60

5	<p>Example 4 was repeated using the following high chloride bath composition with the same concentration of additives and using 40 g/l ferrous sulphate:</p> <table style="margin-left: 40px; border: none;"> <tr> <td style="padding-right: 20px;">nickel sulphate</td> <td>150 g/l</td> </tr> <tr> <td>nickel chloride</td> <td>150 g/l</td> </tr> <tr> <td>boric acid</td> <td>45 g/l</td> </tr> </table>	nickel sulphate	150 g/l	nickel chloride	150 g/l	boric acid	45 g/l	5
nickel sulphate	150 g/l							
nickel chloride	150 g/l							
boric acid	45 g/l							
10	<p>A bright, quite well-leveled deposit with good low current density coverage and with good ductility was obtained.</p>	10						

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nickel sulphate	150 g/l							
nickel chloride	150 g/l							
boric acid	45 g/l							
10	<p>A bright, quite well-leveled deposit with good low current density coverage and with good ductility was obtained.</p>	10						

15 Plating cell—5 litre rectangular cross-section (13 cm x 15 cm) made of "Pyrex". 15  
"Pyrex" is a Trade Mark.

Solution volume—4 litres to give a solution depth, in absence of anode, of about 20.5 cm.

Temperature—55°C. (maintained by immersing cell in a thermostatically controlled water bath).

Agitation—moving cathode rod.

Anode—two titanium baskets, one containing electrolytic nickel and the other

25 stacked "Armco" Iron sheets with an estimated Nickel anode to Iron anode 25  
area ratio of about 10:1. "Armco" is a Trade Mark.

30 polished side of cathode of about 45°—polished side facing anode at an approximate distance of 10.2 cm and scribed vertically in centre with a 1 cm wide band of a single pass of 2/0 grit emery paper scratches. 30

Time—solution electrolyzed about 7 hours per day—occasional cathodes plated for 30 minutes to evaluate deposit levelling, uniformity, ductility, lustre (overall and in low current density recessed area).

Additions—the pH was periodically adjusted when necessary with dilute sulphuric acid to within a range of 3.0 to 3.5 electrometric; periodic re-

plenishment additions of the primary brightener and the secondary auxiliary brightener were made to maintain deposit lustre and levelling. The ferrous iron content of the bath was maintained with separate nickel and "Armco" Iron anode systems in bagged titanium baskets with occasional corrective additions of ferrous sulphate, based on analysis for ferrous iron, to maintain the nickel and ferrous iron contents of the bath fairly constant.

50 electrolysis at a cell current of 5 amperes. The deposits were easily maintained brilliant, well-levelled and ductile at quite low tensile stress. With the vigorous air agitation used a pH of 3.0 to 3.5 at 55°C. and a ferrous sulphate concentration of about 60 g/l appeared to be optimum to give the maximum practical iron concentration of about 40% in the deposit. No substantial darkening of the solution occurred, the anode bags remained clean and uncoated with basic ferric salts and no basic ferric salts could be detected as suspended in the plating bath. 55 The bath during the period of electrolysis was suitably replenished with nickel and "Armco" Iron in the respective titanium baskets to maintain anode area ratio of 10:1. The primary and secondary auxiliary brighteners were also periodically replenished.

60 WHAT WE CLAIM IS:— 60

1. A process for electrodepositing on a substrate an alloy of iron and nickel or an alloy of iron, cobalt and nickel comprising passing an electric current from an



- anode to a cathode through an aqueous acidic plating solution containing at least one ferrous compound and at least one nickel compound with or without at least one cobalt compound, the plating solution also containing at least one compound providing glucoheptonate anion in a concentration of 2 grams per litre to 50 grams per litre.
- 5 2. A process according to claim 1, wherein the plating solution contains nickel sulphate. 5
3. A process according to Claim 1 or Claim 2, wherein the plating solution contains nickel chloride.
- 10 4. A process according to any preceding claim, wherein the plating solution contains nickel sulphamate. 10
5. A process according to any preceding claim, wherein the plating solution contains cobalt sulphate.
- 15 6. A process according to any preceding claim, wherein the plating solution contains cobalt chloride. 15
7. A process according to any preceding claim wherein the plating solution contains cobalt sulphamate.
8. A process according to any preceding claim, wherein the plating solution contains ferrous sulphate and/or ferrous chloride and/or ferrous sulphamate.
- 20 9. A process according to any preceding claim, wherein the plating solution contains at least one compound providing glucoheptonate anion in a concentration of 10 grams per litre to 50 grams per litre. 20
10. A process according to any preceding claim, wherein the plating solution contains one or more additives chosen from:
- 25 (a) primary brighteners; 25  
(b) secondary brighteners;  
(c) secondary auxiliary brighteners;  
(d) anti-pitting agents.
11. A process according to Claim 10, wherein the additive(s) is/are chosen from: sodium saccharinate, sodium allyl sulphonate, 1,4-di-( $\beta$ -hydroxyethoxy)-2-butylene, 1,4-di( $\beta$ -hydroxypropoxy)-2-butyne and sodium lauryl sulphate.
- 30 12. A process according to claim 1 substantially as herein described with particular reference to any one of Examples 4 to 6. 30
13. An electroplated article which has been obtained by the process claimed in any preceding claim. 35
14. An aqueous acidic plating solution as defined in any one of Claims 1 to 11.
15. An aqueous acidic plating solution according to Claim 14 substantially as herein described with particular reference to any one of Examples 4 to 6.

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